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Thermodynamic functions of 2-anilinopyridine from IR and Raman spectra

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Abstract On the basis of vibrational assignments, the thermodynamic functions, namely, the enthalpy, the heat capacity, the free energy and the entropy of 2-anilinopyridine have been calculated at a pressure of 1 atmosphere in the temperature range 100–1500 K under rigid rotor-harmonic oscillator approximation

Keywords Vibrational spectrum, thermodynamic functions, rigid rotor-harmonic oscillator.

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The computation of thermodynamic functions appear to be one of the most important application of IR and laser Raman Spectra of the complex molecules. From the vibrational data obtained from the spectra, Urey [1], Tolman and Badger [2] first suggested that it is quite possible to calculate with accuracy, the values of various thermodynamic functions. This is of great practical importance particularly since the direct experimental measurement of these quantities is quite difficult. The values of the thermodynamic functions calculated from the spectroscopic data are more accurate than the values obtained from the thermal measurements. The thermodynamic function of the molecule 2-anilinopyridine have not been reported so far. With this end in view, the decision to compute the thermodynamic functions, namely, the enthalpy functions $(H^0 - E_0^0)/T$, the heat capacity (C_p^0), the free energy function $[-(G^0 - E_0^0)/T]$ and the entropy function (S^0) was taken for the title molecule at a pressure of 1 atmosphere in the temperature range 100–1500 K under rigid rotor-harmonic oscillator approximation. The frequencies of the different modes of vibrations for the title molecule have been reported by Iseq *et al* [3] and are used for the calculation of the various thermodynamic functions. For the calculations, IBM-PC/AT Computer was used.

The total energy (E) of a system of molecules is given as

$$E = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec}, \quad (1)$$

And the total partition function (Q) can be expressed as the product of the individual partition functions. Hence,

$$Q = Q_{trans} \cdot Q_{rot} \cdot Q_{vib} \cdot Q_{elec}, \quad (2)$$

where the subscripts trans, rot, vib and elec stands for translation, rotational, vibrational and electronic respectively. Also

$$Q = \Sigma g_i \exp(-\epsilon_i/kT), \quad (3)$$

where g_i is the statistical weight of the i-th energy level [4], k is the Boltzmann constant and T is the absolute temperature. Contribution of each partition function may be evaluated separately and then added to the corresponding thermodynamic functions to obtain the total values. The electronic contribution is small and hence ignored. This is

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because ϵ_{elec} is large in comparison to kT at ordinary temperature. The various equations used in the computation of various partition functions and their contribution to different thermodynamic functions are given by Colthup *et al* [5]. The standard expressions [5–7] have been used and their contributions to various thermodynamic functions have been calculated at various temperatures. For determining rotational contributions, following structural parameters were used for 2-anilinopyridine [8–10]

Bond length (Å)		Bond Angle (°)	
N_1–C_2 = 1.36,	C_2–C_3 = 1.42	$N_1C_2C_3$ = 122,	$C_2C_3C_4$ 120
C_3–C_4 = 1.38,	C_4–C_5 = 1.38	$C_3C_4C_5$ = 120,	$C_4C_5C_6$ = 119
C_5–C_6 = 1.42,	C_6–N_1 = 1.36	$C_5C_6N_1$ = 119,	$C_6N_1C_2$ = 120
C_2–N_7 = 1.44,	N_7–C_8 = 1.44	$N_1C_2N_7$ = 119,	$C_3C_2N_7$ = 119
C_8–C_9 = 1.38,	C_9–C_{10} = 1.42	$N_7C_8C_9$ = 120,	$N_7C_8C_{13}$ = 120
C_{10}–C_{11} = 1.37,	C_{11}–C_{12} = 1.37	$C_8C_9C_{10}$ = 121,	$C_9C_{10}C_{11}$ = 119
C_{12}–C_{13} = 1.42,	C_{13}–C_8 = 1.38	$C_{10}C_{11}C_{12}$ = 120,	$C_{11}C_{12}C_{13}$ = 119
		$C_{12}C_{13}C_8$ = 121,	$C_{13}C_8C_9$ = 120
		$C_2N_7C_8$ = 180,	

where C_2 to C_6 are the carbon atoms of the pyridine ring while C_8 to C_{13} are the carbon atoms of the phenyl group in the 2-anilinopyridine molecule. N_1 is the nitrogen atom of the pyridine ring while N_7 is for the imine group. X-axis has been taken perpendicular to the plane of the ring and Z-axis to pass through the $-NHC_6H_5$ group. The symmetry number of the overall rotation is taken as 3 and the internal rotation as 2. The principal moments of inertia are found to be 25.38, 203.86 and 229.24 × 10^{-39} gm cm^2 respectively.

The various thermodynamic functions computed for the 2-anilinopyridine molecule have been shown in Table 1.

The calculation of the thermodynamic functions at various temperatures (100–1500 K) were carried out for one mole of the ideal gas at one atmospheric pressure. The variation of the enthalpy function $[-(H^0 - E_0^0)/T]$ and the heat capacity at constant pressure (C_p^0) with absolute temperature have been shown in the Figure 1 while the variation of the free energy function $[-(F^0 - F_0^0)/T]$ and the entropy (S^0) with absolute temperature have been shown in Figure 2 respectively.

The enthalpy function represent the total energy stored in a system. When a system changes from solid to liquid to gaseous state, the enthalpy of the system increases. Similar trend is reflected from the enthalpy values for 2-anilinopyridine molecule as we increase the temperature in the range 100–1500 K.

The entropy is regarded as the measure of randomness in a system. As the temperature increases, entropy also increases as is shown in Table 1. Similar trend will be followed for the value of free energy and heat capacity for the title molecule under investigation.

Table 1. Thermodynamic functions of 2-anilinopyridine (in cal K^{-1} mol^{-1})

Temp. (K)	$(H^0 - E_0^0)/T$	C_p^0	$-(F^0 - E_0^0)/T$	(S^0)
100	9.341236	51.503421	12.124652	59.012346
200	12.849603	54.086681	20.781823	65.636284
300	16.990803	56.214824	31.686939	72.605627
400	21.191220	58.634513	37.694838	78.825733
500	25.183188	60.611260	44.378131	84.394448
600	28.846481	62.107503	49.240315	89.353983
700	32.145421	63.69731	53.96729	93.755152
800	35.088941	65.069516	57.286201	97.658457
900	37.706215	66.420122	59.900166	101.126377
1000	40.033238	67.914275	62.274419	104.217514
1100	42.106137	69.378212	63.635831	106.984350
1200	43.958214	70.513945	64.980028	109.472159
1300	45.618915	71.600617	66.078636	111.719532
1400	47.113717	72.945355	67.185380	113.759072
1500	48.464421	73.953824	67.940779	115.618245

S^0 = entropy, F^0 = free energy, H^0 = enthalpy, C_p^0 = heat capacity and E^0_0 = zero point energy.

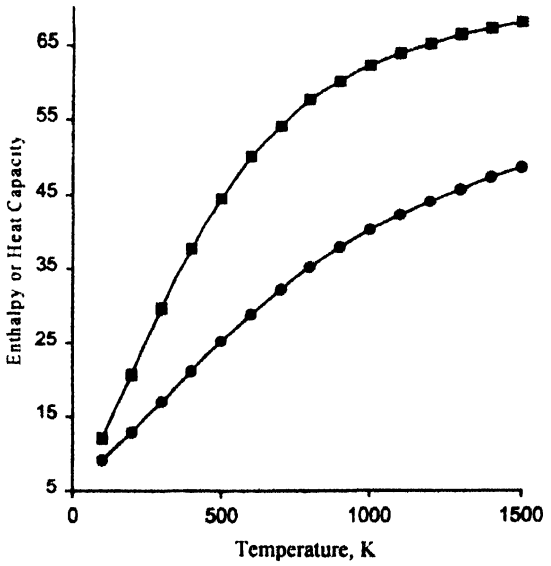

Figure 1. Variation of enthalpy (●)/heat capacity (◆) with temperature for 2-anilinopyridine.

It was also found that the thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range. The variation of these thermodynamic functions with temperature are in

good agreement with the trend reported in the literature [11-18].

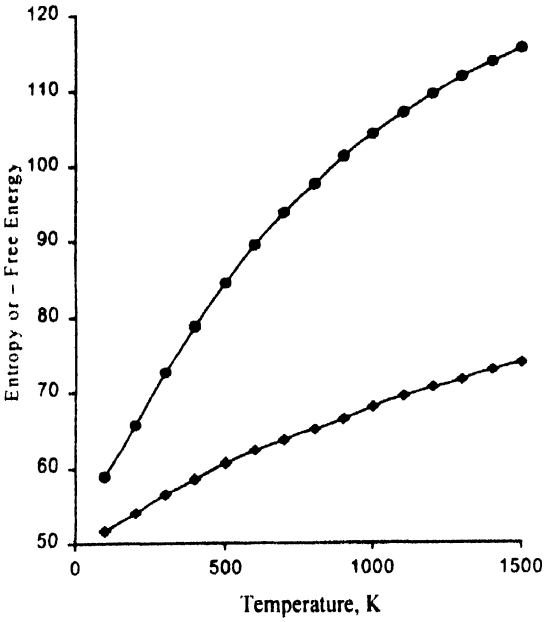

Figure 2. Variation of entropy (●)/free energy (◆) with temperature for 2-anilinopyridine

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References

[1] H C Urey *J Am Chem Soc* **45** 1445 (1923)

[2] R C Tolman and R M Badger *J Am Chem Soc* **45** 2277 (1923)

[3] M Isaq, S P Gupta, S D Sharma and B S Yadav *Orient. J Chem.* **14** 417 (1998)

[4] W J Moore *Physical Chemistry* (Englewood Cliffs . Prentice Hall) (1962)

[5] N B Colthup, L H Daly and S E Wiberley *Introduction to Infrared and Raman Spectroscopy* (New York : Academic) (1964)

[6] L H Herzberg *Molecular Spectra and Molecular Structure* (New York : D Von Nostrand) (1966)

[7] K S Pitzer and W D Gwinn *J A Chem. Phys* **10** 428 (1942)

[8] J C Evans *Spectrochim Acta* **16** 428 [1960]

[9] *Inrteratomic Distances Specal Publication, No II* (The Chemical Society, London) (1958)

[10] *International Tables for X-ray Crystallography Vol-III, Physical and Chemical Tables* (Birmingham, England : Kynoch) (1962)

[11] C L Chaterjee, P P Garg and R M P Jaiswal *Spectrochim Acta* **34A** 943 (1978)

[12] R K Goel and M L Agarwal *Spectrochim Acta* **38A** 583 (1982)

[13] R K Goel and M L Agarwal *J. De. Chimie Physiq.* 79 765 (1982)

[14] S G Frankiss, D J Harrison and W Kynaston *Spectrochim Acta* **30A** 1225 (1974)

[15] R K Gupta, R Prasad, Krishan Lal and Hari L Bhatnagar *Indian J Phys* **60B** 7 (1986)

[16] B S Yadav, Vir Singh and Vipin Kumar *J. Insts Chemists* **69** 5 (1997)

[17] B S Yadav, Vipin Kumar and M K Yadav *Indian J Pure Appl. Phys.* **36** 557 (1998)

[18] V K Rastogi, M Alcolea Palafox, B Lal and Vaibhav Jain *Indian J Pure Appl Phys* **38** 564 (2000)